LALIT NARAYAN MITHILA UNIVERSITY
KAMESHWARNAGAR, DARBHANGA

Department of Physics
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SYNOPSIS
of the
Ph.D. thesis entitled

Study of Magnetic Properties and Electronic Structure of Graphene based 2-D Materials.

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1. Introduction:-

The emergence of graphene, a two-dimensional form of carbon, has sparked significant interest among experts in condensed matter physics and materials science. [1] This is primarily due to its exceptional characteristics, including high carrier mobility and the ability to adjust carrier concentration through gating. Despite its potential, graphene's future applications are limited by its status as a zero-band gap semiconductor and its nonmagnetic nature. [2]

Three-dimensional (3-D) layered materials are composed of individual atomic layers stacked upon one another. A defining characteristic of these materials is the presence of strong in-plane chemical bonds. However, there is a weak coupling between the layers, which can be attributed to interactions such as van der Waals forces or hydrogen bonds. This material study includes a wide range of materials, including graphite, clays, ceramics, oxides, halides, chalcogenides, and MAX phases [19]. These materials can be cleaved layer by layer, resulting in their corresponding two-dimensional (2-D) monolayer counterparts. For a long time, the existence of two-dimensional (2-D) materials was considered impossible due to well-established theoretical concepts. The prevailing notion was that 2-D materials are intrinsically unstable and susceptible to thermal and quantum fluctuations [3, 4].

The field of 2D materials gained renewed attention in 2004, when Novoselov and Geim successfully synthesized graphene, a 2-D allotrope of carbon, using the Scotch tape method to mechanically exfoliate graphite.[5–7] The field of 2-D materials has undergone rapid advancement since the discovery of graphene, making it a prominent area of research. The availability of various exfoliation techniques, such as micromechanical cleavage, ion interaction, and surface-assisted ultrasonication, has facilitated the production of 2-D materials with monoatomic layer thickness.

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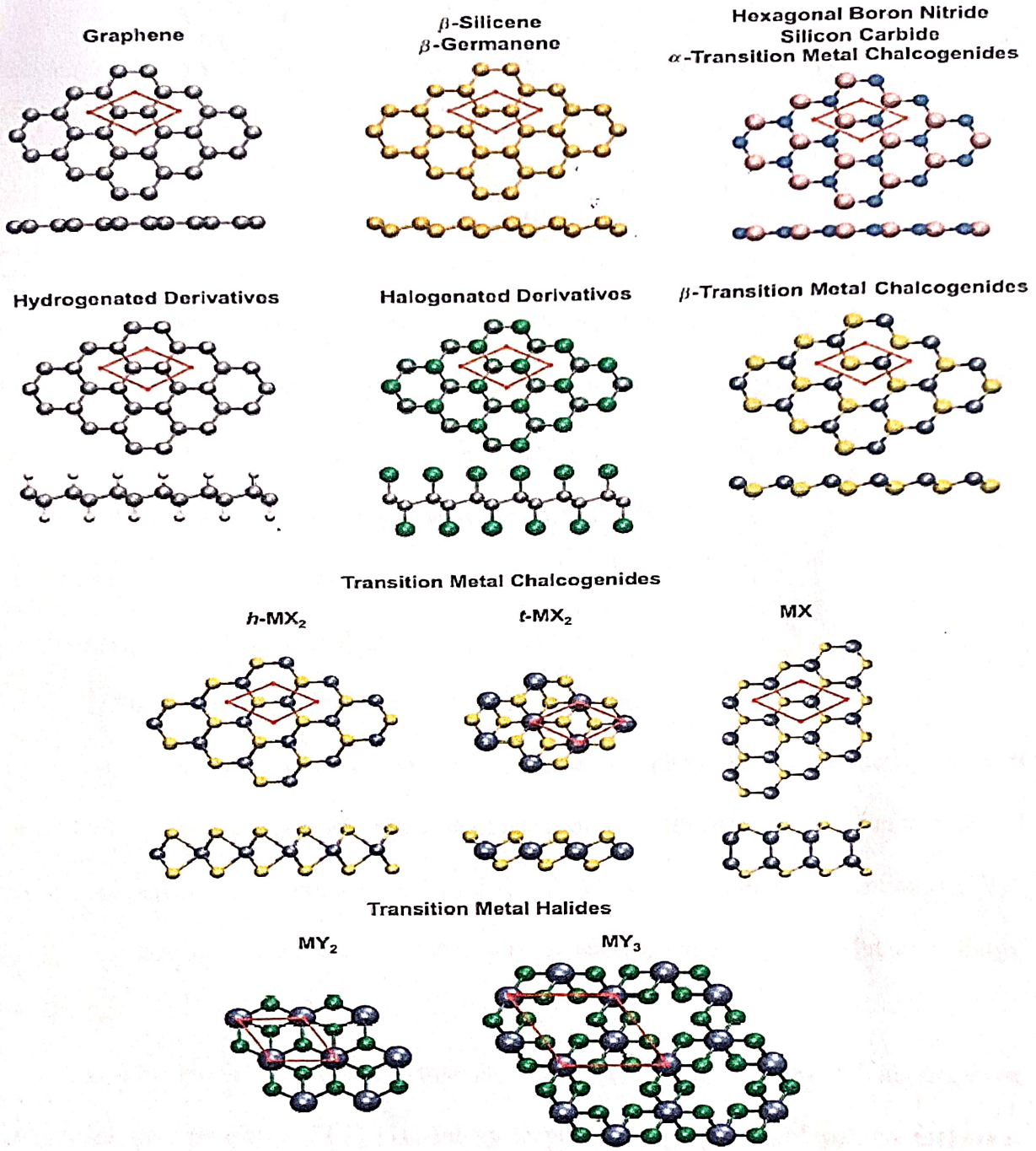

Figure 1.1: Structure of thin 2D materials: graphene, silicene, germanene (and their derivatives), silicon carbide (SiC), hexagonal boron nitride (h-BN) and **α,β** transition metal chalcogenides (TMC) (top). Ultrathin 2D materials such as transition metal chalcogenides (TMC) (center) and halides (TMH)(bottom). Unit cells are depicted in red. Color code: metals in ice blue, halides in green, chalcogenides in yellow, nitrogen in blue, carbon in grey, silicon, and germanium in gold, boron in pink, and hydrogen in white. (Figure adapted from Ref[8]).

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These 2-D materials are hexagonal boron nitride, silicon carbide, transition metal dichalcogenides, and halides. Theoretical simulations backed by robust first principles methods like density functional theory have also contributed to the exploration of numerous other 2-D materials. Figure 1.1 shows a concise visual representation of the 2-D material family.

My research primarily focuses on computationally exploring methods to customize the electronic and magnetic characteristics of graphene-based systems. Using ab-initio calculations based on density functional theory (DFT) and a model Hamiltonian approach [9], we have explored deeply into three variations of graphene derivatives:

a) Adatom-bilayer graphene assembly.

b) 0-D graphene nanoflakes

c) Transition metal atom decorated holey graphene.

Our objective is to understand how magnetic moments form and whether we can adjust these properties externally. Findings of research will emphasize that we can induce and manipulate magnetism in graphene and its derivatives through external interventions such as gating, engineering substrates, or chemically modifying them by introducing foreign atoms.[10]

Another crucial aspect of contemporary graphene research involves utilizing graphene in a field-effect transistor (FET) [11] set up to probe the properties of various materials. Inspired by recent experiments that employed graphene FETs to assess the out-of-plane polarization on the TiO_2-terminated surface of strontium titanate ($SrTiO_3$), our investigation will focus on the graphene/$SrTiO_3$ composite heterostructure. [12] Goal of this research is to decode the microscopic mechanisms underlying surface polarization formation, assess how the presence of graphene affects surface polarizability, and examine the impact of an external electric field on modulating surface polarization values. [13] It is anticipated that the

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computational findings found from this research will serve as a robust foundation and practical roadmap for exploring novel functionalities of graphene derivatives and composite structures in future endeavors.

2. Review of literature and current status in the field in which the proposed work is undertaken:-

'Novoselov et al.'[14], In their pioneering work, Novoselov et al. made significant contributions to the field of graphene research. They demonstrated the remarkable properties of graphene, a single layer of carbon atoms arranged in a hexagonal lattice. These properties include high strength, excellent electrical and thermal conductivity, and unique optical properties. Novoselov et al.' also highlighted the potential applications of graphene, such as in corrosion-resistant coatings for offshore structures. Novoselov et al. reviewed the synthesis methods of graphene, including chemical vapor deposition and mechanical exfoliation, and calculated the properties and potential applications of graphene-based materials in a variety of fields. Furthermore, Novoselov et al. provided insights into the structural analysis of giant fullerenes composed of 100 or more cage carbons.

'Wang, Changchun, et al.' [15], Graphene, a two-dimensional material composed of carbon atoms arranged in a honeycomb lattice, has attracted significant attention due to its unique physical and chemical properties that make it suitable for a wide range of applications. One of the key properties of graphene is its exceptional electronic structure. A comprehensive review of the structural analysis of giant fullerenes composed of 100 or more cage carbons was presented by Wang and co-workers. They highlighted the challenges in synthesizing, purifying, and determining the structures of these large cage carbons due to their low yield, poor solubility, and numerous possibilities of cage isomerization. In recent years, there has

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been growing exploration in the field of nanotechnology, leading to the identification of unique properties of nanomaterials compared to conventional formulations of the same material.

'Yue, Wenxuan, et al'.[16] investigated the electronic and magnetic properties of graphene (0001) interfaces using density functional theory (DFT). Their study provides valuable insights into the behavior of these interfaces, shedding light on potential applications in spintronics and magnetic storage devices. By employing advanced computational techniques, the Researcher contribute to the understanding of graphene-based heterostructures and their interactions with transition metal substrates. This research expands the knowledge base in the field of materials science and nanotechnology, offering guidance for future studies aimed at harnessing the unique properties of graphene in magnetic systems.

Li et al. [17], explore pyridinic nitrogen doping as a versatile strategy for precisely manipulating the structure-property relationships of nanographenes. Published in Chemistry of Materials, their research delves into the intricate effects of nitrogen incorporation on the properties of nanographenes, offering insights into their electronic structure, optical properties, and chemical reactivity. By elucidating the role of pyridinic nitrogen doping, this study contributes to advancing the design and synthesis of tailored nanographene materials with enhanced functionalities for various applications in electronics, optoelectronics, and catalysis.

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3. Objective /Significance of proposed work:-

1. Using Density functional theory, we will investigate the effect of metal atom adsorption on the electronic properties of bilayer graphene with the aim to understand formation of local magnetic moments within the system.
2. To study the electronic and magnetic properties of nanographene.
3. To study the effect of an external electric field applied normally to the graphene-$SrTiO_3$ geometry and its directionality on the surface polarization will also be studied with the aim of tuning the electric polarization by external means.
4. Employing density functional theory, we will study the electronic properties of nitrogenated holey-graphene (C_2N) systems and a C_2CF system obtained by substitution of N atoms in the C_2N geometry with a C-F molecule.

3. Plan of work/materials and methods/technical programmes:-

An exploration of the electronic and magnetic properties of graphene-based systems through a variety of methods and techniques Depending on the physical specifications of the system. In our study, we have selected the ab-initio density functional techniques and the Hamiltonian approaches [18] which will be used to solve the exact diagonalization scheme. Ab-initio density functional techniques refer to computational methods used in quantum mechanics to calculate the electronic structure of atoms, molecules, and materials from first principles, without relying on empirical parameters. These techniques are based on the density functional theory (DFT), where the electronic density serves as the key variable instead of wavefunctions. Ab-initio methods solve the Kohn-Sham equations to determine the electronic structure, energy, and properties of the system. They are widely used in materials science, chemistry, and physics to predict and understand the behavior of complex systems at

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the atomic and molecular levels. Kohn and Sham introduced a formulation in 1965, based on the Hohenberg-Kohn theorems, that approximated the kinetic energy functional $\check{T}(\rho)$ for an interacting electron system. This approximation was achieved by representing the interacting system with a non-interacting electron system that shares the same ground state charge density $\rho(\mathbf{r})$. [20] The total energy for system of N interacting electrons with charge density $\rho(r)$ can be written as $E[\rho] = F[\rho] + \int \hat{V}_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}$. with the universal functional $F[\rho]$ for the system given by $F[\rho] = T[\rho] + V_H[\rho] + E_{xc}[\rho]$.

The kinetic energy of the interacting electron can be represented as $T[\rho]$. The electrostatic Coulomb energy of electrons, also known as the Hartree term, is denoted as $V_H[\rho]$. Additionally, $E_{xc}[\rho]$ encompasses all exchange and correlation effects.

By approximating the kinetic and exchange-correlation functionals, it is possible to map a system of interacting electrons onto an equivalent system of non-interacting electrons moving in an effective potential generated by the other electrons and having the same electron density $\rho(r)$. This transformation reduces the complex interacting many-electron problem to a set of self-consistent non-interacting one-electron equations called the Kohn-Sham equations.

Despite the different approaches employed by various methods in their formulation, they all share the common goal of solving the fundamental many-body Hamiltonian, which serves as the comprehensive description of all forms of matter.

Matter, consisting of atoms, exhibits properties that arise from the diverse interactions among these atoms. In quantum mechanics, the behavior of a group of atoms at the microscopic level is determined by the interactions between electrons and nuclei, which are the fundamental particles that make up an atom. These interactions take place through electrostatic forces, such as Coulomb forces. Therefore, in general, any physical state of

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matter, be it solid, liquid, or gaseous, can be represented by the many-body Hamiltonian, which is given by Equation 1.1.

$$\hat{H} = -\sum_{I}^{N_a} \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_{i}^{N_e} \frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{e^2}{2} \sum_{I=1}^{N_a} \sum_{J \neq I}^{N_a} \frac{Z_I Z_J}{|R_I - R_J|} + \frac{e^2}{2} \sum_{i=1}^{N_e} \sum_{j \neq i}^{N_e} \frac{1}{|r_i - r_j|} - e^2 \sum_{I=1}^{N_a} \sum_{i=1}^{N_e} \frac{Z_I}{|R_I - r_i|} \quad ..1.1$$

M_I and m_i are the nuclear and Z_I and e are the electron masses respectively. where $\{R_I\}$, Nuclear coordinates are represented by $I = 1,.., N_a$ and $\{r_i\}$, $i = 1,...,N_e$ are the set of N_e electron coordinates.

5. Facility available at the place of work/relevance to the proposal: -

This theoretical research work involves computer programming and simulation. It can be conveniently conducted on a personal computer with internet connectivity. The university Department of Physics and an ARC (Advanced Research Center)has a modern computer laboratory with internet access. The required DFT software for carrying out this work and the simulation process will be done. In addition to that, there is a departmental library that has a comprehensive collection of books on Material science, Nanotechnology, Quantum Mechanics, and electronics, which will same as valuable resources for this research. Furthermore, essential data can be efficiently gathered from the internet and stored on the personal computer, and necessary journals can be easily accessed and procured through numerous websites. Some relevant books are also available in the central library of L.N. Mithila University, Darbhanga.

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